Journal of Vacuum Science & Technology B

Electrochemically etched Ni tips in a constant-current mode for spin-polarized scanning tunneling microscopy

Hui Chen, Wende Xiao, Xu Wu, Kai Yang, and Hong-Jun Gao

Citation: Journal of Vacuum Science & Technology B **32**, 061801 (2014); doi: 10.1116/1.4898865
View online: http://dx.doi.org/10.1116/1.4898865
View Table of Contents: http://scitation.aip.org/content/avs/journal/jvstb/32/6?ver=pdfcov
Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Electrochemically etched Ni tips in a constant-current mode for spin-polarized scanning tunneling microscopy

Hui Chen, Wende Xiao,[a)] Xu Wu, Kai Yang, and Hong-Jun Gao[b)]
Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

(Received 24 July 2014; accepted 10 October 2014; published 22 October 2014)

The authors present an efficient method to fabricate Ni tips for spin-polarized scanning tunneling microscopy (SP-STM) via electrochemical etching of Ni wires in a constant-current mode. Instead of applying constant voltages to trigger the electrochemical etching of Ni wires in previous reports, here a constant current is applied, which ensures a stable etching process and favors a high yield of Ni tips with good quality. The prepared Ni tips have been applied to obtain atomic resolution images on various surfaces in conventional STM measurements and to resolve magnetic-state-dependent contrast of Co islands grown on a Cu(111) surface in SP-STM experiments. © *2014 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4898865]

I. INTRODUCTION

Spin-polarized scanning tunneling microscopy (SP-STM) is a state-of-the-art technique that allows us to study the spin texture of low-dimensional nanostructures at an atomic level.[1,2] As the SP-STM systems essentially measure the spin-polarized tunneling current between the conducting samples and the metallic tips, their performance strongly depends on the tips.[3–5] An ideal SP-STM tip should offer simultaneously a high spatial resolution down to the atomic level and a high spin polarization with tunable spin orientation and negligible magnetic stray field.[6] Many methods have been employed to produce optimal SP-STM tips over the years. For instance, ferromagnetic tips of Fe and Ni (Refs. 7–9) and antiferromagnetic tips of Cr and MnNi (Ref. 10) were produced via electrochemical etching of polycrystalline bulk materials. Nonmagnetic tips coated with magnetic thin films were also prepared for SP-STM measurements.[2,6,11,12] However, as Cr and MnNi are very hard and brittle, several steps are required to produce sharp tips with uniform shapes from bulk Cr and MnNi rods or foils.[13,14] The fabrication of magnetic-thin-film-coated nonmagnetic tips is also very complicated and time-consuming.[15] In addition, these thin-film-coated tips are very fragile against unavoidable tip-conditioning during SP-STM measurements.[15] Therefore, Ni tips made from polycrystalline Ni wires are widely used in SP-STM due to their cheapness, easy preparation and stability against oxidization in air, despite of possible magnetic stray field.

In previous reports, Ni tips were usually prepared by "drop-off" electrochemical etching of polycrystalline Ni wires in a constant-voltage mode,[8,16,17] in which a constant dc voltage was commonly applied to the anode (Ni wire) and ring-shaped Pt cathode.[16] A lamella of KCl solution suspended inside the Pt ring was used as the electrolyte. As the volume of the lamella was rather small and its thickness kept deducing due to water evaporation during the electrochemical etching process, the concentration of the etchant varied and $NiCl_2$ salts formed around the electrodes, leading to the variation of the etching current.[16] As the etching current indicates the whole amount of charge carriers supplied to the anode per second and strictly determines the etching rate, the variation of current suggests an unstable etching process, which might result in a low yield of high-quality Ni tips.[18]

Herein, we report on the efficient fabrication of Ni tips for SP-STM via electrochemical etching of Ni wires in a constant-current mode, which ensures a stable etching process and favors a high yield of Ni tips with good quality. The prepared Ni tips routinely offer an atomic resolution of conducting surfaces in conventional STM measurements as well as a spin-dependent magnetic resolution of nanoscale systems in SP-STM measurements.

II. EXPERIMENT

The setup for electrochemical fabrication of Ni tips is schematically shown in Fig. 1(a). A Pt ring with a diameter of ∼50 mm acting as the cathode electrode was immersed in a beaker filled with 7.2% HCl aqueous solution. The anode electrode of a Ni wire with a diameter of 0.5 mm (Ni 99.9% GoodFellow Co.) was clamped and threaded at the center through the Pt ring. The length of the Ni wire under the ring is ∼4 mm. A commercial dc power supplier (maximum output voltage of 36 V and maximum output current of 20 A) operated in the constant current mode was applied to trigger the electrochemical reaction. In 7.2% HCl aqueous solution,

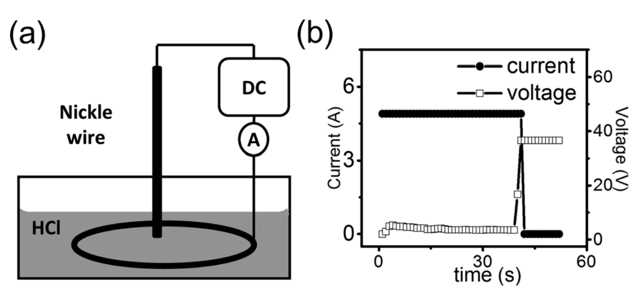

FIG. 1. (a) Schematic diagram of the setup for the tip preparation. (b) Variation of the current and voltage vs time in the etching process.

a)Electronic mail: wdxiao@iphy.ac.cn
b)Electronic mail: hjgao@iphy.ac.cn

 2166-2746/2014/32(6)/061801/3/$30.00

Ni oxidation is thermodynamically favored compared to water oxidation.[16]

Once an optimal constant current of 4.9 A was passing through the electrolyte, the etching process started and the voltage applied to the electrodes varied, as shown in Fig. 1(b). As the current was hundreds of times higher than that in previous reports, the electrochemical reaction was intense at the etching position of the Ni wire. A regular flow of the electrolyte from the Ni wire to the beaker took the $NiCl_2$ product away from the Ni wire. Thus, no $NiCl_2$ salt aggregated around the Ni wire and Pt ring, different from previous reports.[16] At the end of the process, the current suddenly dropped to zero and a "drop-off" appeared [Fig. 1(b)]. In the meantime, the voltage jumped to ~36 V (the maximum output voltage of the power supplier), as the resistance went to infinity. Ni tips with sharp apex could be eventually fabricated at the breaking point. The whole etching process took about 40 s [Fig. 1(b)], much shorter than previous reports of ~2 min.[16] After the electrochemical etching, the Ni tips were first rinsed in distilled water in order to eliminate $NiCl_2$ formed during the etching process and then in alcohol to remove organic contaminants.

Figure 2(a) shows an optical microscopy (OM) image of a typical Ni tip prepared by the constant-current method. Figure 2(b) illustrates a scanning electronic microscopy (SEM) image around the tip apex. It is seen that the surface of the Ni tip is very smooth and the radius of the tip apex is ~30 nm, comparable to that of W tips prepared in a similar procedure.[3,19]

III. RESULTS AND DISCUSSION

The performance of the prepared Ni tips has been tested with several STM systems in different environments. Figure 3(a) shows an atomic resolution STM image of an HOPG surface obtained with a home-made STM in air at room temperature using a Ni tip that was prepared a month ago. Figure 3(b) shows an STM image of a clean Au(111) surface acquired with an ultrahigh vacuum (base pressure $< 1 \times 10^{-10}$ mbar) low temperature (4.2 K) STM (Unisoku) equipped with superconducting magnets.[20–22] The atomic resolution of the Au(111) surface is clearly seen. The capability to routinely obtain atomic resolution images on various surfaces indicates that the prepared Ni tips are very sharp and stable for STM measurements, providing themselves as suitable alternative to the commonly used W and Pt/Ir tips.

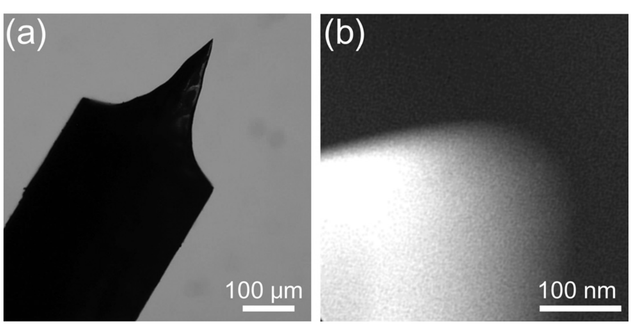

FIG. 2. (a) OM image of an as-prepared Ni tip. (b) Highly magnified SEM image of the same tip showing a tip apex of ~30 nm.

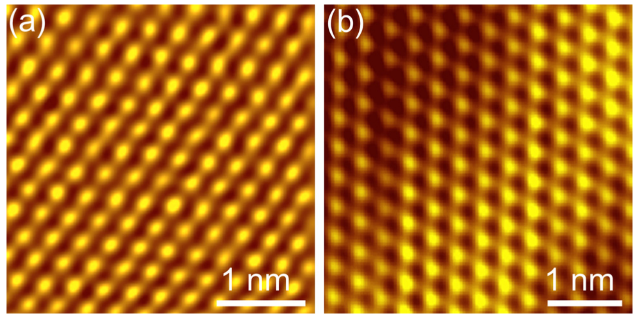

FIG. 3. (Color online) (a) Atomic resolution STM image of an HOPG surface (2.5 × 2.5 nm) acquired at room temperature in air. Sample bias: U = −1.5 V; tunneling current I = 0.1 nA. (b) Atomic resolution STM image of an Au(111) surface (3.0 × 3.0 nm) acquired at 4.2 K in ultrahigh vacuum (U = −0.2 V and I = 0.5 nA).

The prepared Ni tips have been successfully used to perform SP-STM measurements of Co islands grown on Cu(111) surface. Prior to the transfer of the sample into the STM head, the Ni tip is magnetized *in situ* along its axis in a field of 0.3 T by means of a superconducting magnet.[7] Deposition of Co atoms on Cu(111) surface at room temperature results in the formation of triangular Co islands,[10,11] as seen in the topographic image shown in Fig. 4(a). Two different orientations of the triangular islands are observed, rotated by 180° with respect to each other. According to the literatures, the different island orientation is due to different (faulted and unfaulted) stacking of Co atoms with respect to the Cu(111) surface.[11] Each Co island exhibits an out-of-plane magnetic polarization, either upward or downward.[7] Figure 4(b) illustrates the differential tunneling conductance

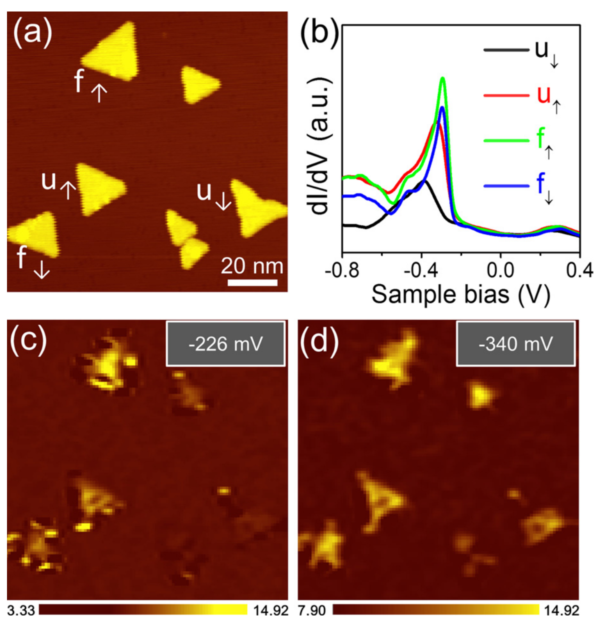

FIG. 4. (Color online) (a) Topographic image of Co islands grown on Cu(111). Four types of Co islands are distinguished according to their stacking with respect to the substrate (faulted or unfaulted) and their spin directions (up or down), as indicated by $u_\uparrow$, $u_\downarrow$, $f_\uparrow$, and $f_\downarrow$, respectively. (b) Spin-resolved tunneling spectra on four Co islands marked in (a). (c) and (d) Simultaneously acquired fixed-bias closed-loop dI/dV mapping over the same region as (a) at the indicated bias voltages.

(dI/dV) spectra acquired on four Co islands labeled in Fig. 4(a). The Co islands show stacking- and magnetic-state-dependent dI/dV spectra, in line with previous SP-STM study using a W tip coated with Cr film.[7] Careful analysis reveals that Co islands with the same stacking and spin polarization show almost identical dI/dV spectra, despite of different island sizes or inhomogeneity. Figures 4(c) and 4(d) show the dI/dV maps acquired on the same area shown in Fig. 4(a) with sample biases of −226 and −340 mV, respectively. Although the standing wave patterns of the free electrons due to the quantum confinement of the Co islands[12,23] may blur the contrast among the Co islands, these dI/dV maps straightforwardly demonstrate the stacking- and magnetic-state-dependent contrast of Co islands, akin to previous reports.[11,12,23]

IV. CONCLUSIONS

We have shown that Ni tips can be efficiently fabricated via electrochemical etching of Ni wires in a constant-current mode. The constant current ensures a stable etching process and favors a high yield of Ni tips that are suitable for conventional STM and SP-STM experiments.

ACKNOWLEDGMENTS

Financial support from MOST (Grant No. 2011CB932700), NSFC (Grant No. 61390501), and CAS in China is acknowledged.

[1]M. Bode, Rep. Prog. Phys. **66**, 523 (2003).
[2]R. Wiesendanger, Rev. Mod. Phys. **81**, 1495 (2009).
[3]J. P. Ibe, J. Vac. Sci. Technol., A **8**, 3570 (1990).
[4]I. H. Musselman, J. Vac. Sci. Technol., A **8**, 3558 (1990).
[5]T. T. J. Lindahl and L. Montelius, J. Vac. Sci. Technol., B **16**, 3077 (1998).
[6]R. Wiesendanger, Curr. Opin. Solid State Mater. Sci. **15**, 1 (2011).
[7]M. V. Rastei and J. P. Bucher, J. Phys.: Condens. Matter **18**, L619 (2006).
[8]C. Albonetti, M. Cavallini, M. Massi, J. F. Moulin, and F. Biscarini, J. Vac. Sci. Technol., B **23**, 2564 (2005).
[9]K. Schouteden, D. A. Muzychenko, and C. Van Haesendonck, J. Nanosci. Nanotechnol. **8**, 3616 (2008).
[10]S. Murphy, J. Osing, and I. Shvets, Appl. Surf. Sci. **144-145**, 497 (1999).
[11]O. Pietzsch, A. Kubetzka, M. Bode, and R. Wiesendanger, Phys. Rev. Lett. **92**, 057202 (2004).
[12]O. Pietzsch, S. Okatov, A. Kubetzka, M. Bode, S. Heinze, A. Lichtenstein, and R. Wiesendanger, Phys. Rev. Lett. **96**, 237203 (2006).
[13]A. Li Bassi *et al.*, Appl. Phys. Lett. **91**, 173120 (2007).
[14]A. Schlenhoff, S. Krause, G. Herzog, and R. Wiesendanger, Appl. Phys. Lett. **97**, 083104 (2010).
[15]M. Bode, M. Getzlaff, and R. Wiesendanger, Phys. Rev. Lett. **81**, 4256 (1998).
[16]M. Cavallini and F. Biscarini, Rev. Sci. Instrum. **71**, 4457 (2000).
[17]Y. P. T. Gnanavel, X. Xu, B. J. Inkson, M. R. J. Gibbs, and G. Möbus, J. Phys.: Conf. Ser. **126**, 012071 (2008).
[18]G. Xu, Z. Liu, K. Xu, Y. Zhang, H. Zhong, Y. Fan, and Z. Huang, Rev. Sci. Instrum. **83**, 103708 (2012).
[19]B. F. Ju, Y. L. Chen, and Y. Ge, Rev. Sci. Instrum. **82**, 013707 (2011).
[20]L. Liu *et al.*, Sci. Rep. **3**, 1210 (2013).
[21]K. Yang, W. Xiao, L. Liu, X. Fei, H. Chen, S. Du, and H.-J. Gao, Nano Res. **7**, 79 (2014).
[22]J. Mao, H. Zhang, Y. Jiang, Y. Pan, M. Gao, W. Xiao, and H.-J. Gao, J. Am. Chem. Soc. **131**, 14136 (2009).
[23]H. Oka, P. A. Ignatiev, S. Wedekind, G. Rodary, L. Niebergall, V. S. Stepanyuk, D. Sander, and J. Kirschner, Science **327**, 843 (2010).